

RESIN COMPOSITION

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Abstract of JP 2003292790 (A)

PROBLEM TO BE SOLVED: To obtain a resin composition having excellent mechanical strengths, light resistance and ageing resistance. ; **SOLUTION:** This resin composition is characterized by containing composite particle powder which has an average particle diameter of 0.01 to 10.0 [μ m] and is prepared by coating the particle surfaces of zinc oxide particle powder with an organosilane compound or a polysiloxane produced from an alkoxysilane and then adhering carbon black to the coating film, wherein the carbon black is adhered in an amount of 1 to 100 pts.wt. per 100 pts.wt. of the zinc oxide particle powder. ; **COPYRIGHT:** (C)2004,JPO

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JP 2003-292790

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Notes:

1. Untranslatable words are replaced with asterisks (* **).
2. Texts in the figure are not translated and shown as is.

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Dictionary: Last updated 06/08/2009 / Priority: 1. Chemistry / 2. Natural sciences / 3. Technical term

FULL CONTENTS

[Claim(s)]

[Claim 1] It is the composite particle powder which is the mean particle diameter of 0.01-10.0 micrometers in which a particle surface of zinc oxide particle powder is covered with an organosilane compound or polysiloxane generated from alkoxysilane, and carbon black has adhered to this covering. A resin composition, wherein coating weight of said carbon black contains composite particle powder which is one to 100 weight section to said zinc oxide particle powder 100 weight section.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention provides the resin composition excellent in mechanical strength, lightfastness, and aging resistance.

[0002]

[Description of the Prior Art] Conventionally, zinc oxide (zinc white) and carbon black are used for resin compositions, such as rubber and plastics, as a vulcanization accelerator or a reinforcer.

[0003] Since zinc oxide absorbs the light of ultraviolet radiation, having the ultraviolet screening effect is known. However, have a catalysis of photooxidation, and change in color of other pigments in a resin composition is promoted, and it has the problem of promoting aging of a resin composition.

[0004] It is known that carbon black will be useful for improvement in the lightfastness of polyethylene as an anti-oxidant.

On the other hand, difficult [dispersion into a resin composition], since grain sizes are the particles which are the mean particle diameter of about 0.005-0.05 micrometer, since bulk densities are a 0.1 g/cm³ grade and bulky powder, handling has the problem that it is difficult and workability is bad.

[0005] Then, additives, such as a reinforcer, are uniformly distributed in the resin composition, and the resin composition excellent in mechanical strength, lightfastness, and aging resistance is called for strongly.

[0006] the resin composition (JP, 2000-319128, A.) which blended until now the zinc oxide etc. which were covered with the silica system substance etc. for the purpose of inhibition

of surface activity The zinc oxide particle powder (JP,H7-187674,A, JP,H8-59890,A, etc.) etc. with which JP,2001-58821,A and a particle surface were covered by polysiloxane or the coupling agent are proposed.

[0007]

[Problem to be solved by the invention]Additives, such as a reinforcer, are uniformly distributed in the resin composition, and the resin composition excellent in mechanical strength, lightfastness, and aging resistance is not yet obtained, although it is just going to be demanded most now.

[0008]namely, the above, although a particle surface is covered with a silica system substance or zinc silicates, such as silica and alkyl modified silica, etc., [zinc oxide JP,2000-319218,A and given in JP,2001-11339,A] Since it is insufficient as an effect which controls surface activity, the resin composition obtained using these does not have sufficient aging resistance.

[0009]the above, although a particle surface is covered with methyl hydrogen polysiloxane or a silane coupling agent, [zinc oxide JP,H7-187674,A and given in JP,H8-59890,A] Since it is insufficient as an effect which controls surface activity, the resin composition obtained using these does not have sufficient aging resistance.

[0010][JP,H11-323174,A] Although the organosilane compound generated from alkoxy silane is covered by the particle surface of black-iron-oxide particle powder or black hydrous iron oxide particle powder and the iron system black composite particle powder in which carbon black fine particle powder has adhered to this organosilane compound covering is indicated, When it blends into a resin composition, a reinforcing effect is weak, and it is difficult to obtain the resin composition excellent in mechanical strength.

[0011]Then, additives, such as a reinforcer, are uniformly distributed in the resin composition, and this invention makes it a technical problem to provide the resin composition excellent in mechanical strength, lightfastness, and aging resistance.

[0012]

[Means for Solving the Problem]This invention as follows can attain said technical problem.

[0013]Namely, this invention is composite particle powder which is the mean particle diameter of 0.01-10.0 micrometers in which a particle surface of zinc oxide particle powder is covered with an organosilane compound or polysiloxane generated from alkoxy silane, and carbon black has adhered to this covering. Coating weight of said carbon black is a resin composition containing composite particle powder which is one to 100 weight section to said zinc oxide particle powder 100 weight section.

[0014]It will be as follows if composition of this invention is explained in more detail.

[0015]A resin composition concerning this invention contains an organosilane compound generated from alkoxy silane to a particle surface of zinc oxide grains which are core particles, or composite particle powder in which polysiloxane coating is carried out and carbon black has adhered to this covering.

[0016]First, composite particle powder in this invention is described.

[0017]Particle shape of zinc oxide particle powder in this invention may be which shape, such as a globular shape, grain form, the shape of a polyhedron, a needle, a spindle shape, rice grain shape, flaky, [scaly, tabular].

[0018]0.009-9.95 micrometers of mean particle diameter [0.014-7.45 micrometers of] of

grain size of zinc oxide grains are 0.019-4.95 micrometers more preferably.

[0019]When mean particle diameter exceeds 9.95 micrometers, since mechanical strength falls, a resin composition produced by composite particle powder obtained serving as a coarse particle, and blending this is not preferred.

[0020]A BET specific surface area value of zinc oxide particle powder is more than $0.5\text{-m}^2/\text{g}$. When a BET specific surface area value is less than $0.5\text{-m}^2/\text{g}$, Since mechanical strength falls, a resin composition produced by zinc oxide grains being big and rough, or having become the grains which sintering produced grains and between grains, and composite particle powder obtained also serving as a coarse particle, and blending this is not preferred. When mechanical strength of a resin composition obtained is taken into consideration, a BET specific surface area value of zinc oxide particle powder of more than $1.0\text{-m}^2/\text{g}$ is more than $1.5\text{-m}^2/\text{g}$ more preferably. If uniform coating treatment by alkoxy silane or polysiloxane to a particle surface of zinc oxide grains and uniform adhesion treatment by carbon black are taken into consideration, the upper limit is $500\text{m}^2/\text{g}$ -- desirable -- $400\text{m}^2/\text{g}$ -- it is $300\text{m}^2/\text{g}$ more preferably.

[0021]a lower limit of a ΔE value usually exceeds 5.0 with a valuation method which the lightfastness of zinc oxide grains mentions later -- upper limit -- 12.0 -- desirable -- 11.0 -- it is 10.0 more preferably.

[0022]Coatings in this invention are an organosilane compound generated from alkoxy silane denoted by ** 1 and polysiloxane denoted by ** 2, conversion polysiloxane denoted by ** 3, end conversion polysiloxane denoted by ** 4, or these mixtures.

[0023]

[Chemical formula 1]



R : $-\text{C}_6\text{H}_5$, $-(\text{CH}_3)_2\text{CHCH}_2$, $-n-\text{C}_m\text{H}_{2m+1}$

X : $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$

m : 1 ~ 18 の整数

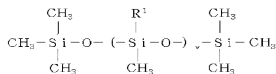
a : 0 ~ 3 の整数

[0024]As alkoxy silane, specifically Methyltriethoxysilane, Dimethyldiethoxysilane, phenyltriethoxysilane, diphenyl diethoxysilane, Dimethyldimethoxysilane, methyl trimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, isobutyl trimethoxysilane, decyltrimethoxysilane, etc. are mentioned.

[0025]If bond strength of carbon black to a particle surface of zinc oxide grains is taken into consideration, Methyltriethoxysilane, methyl trimethoxysilane, dimethyldimethoxysilane, An organosilane compound generated from isobutyl trimethoxysilane and phenyltriethoxysilane is more preferred, and it is an organosilane compound most preferably generated from methyltriethoxysilane, methyl trimethoxysilane, and phenyltriethoxysilane.

[0026]

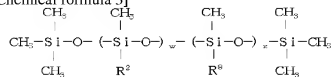
[Chemical formula 2]



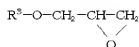
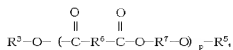
$\text{R}^1: \text{H}, \text{CH}_3 \quad w: 1.5 \sim 4.50$

[0027]

[Chemical formula 3]



$\text{R}^2: \text{R}^5-\text{O}-(-\text{CH}_2-\text{CH}-\text{O})_q-\text{R}^5,$



$\text{R}^3, \text{R}^6, \text{R}^7: -(\text{CH}_2)_1-$

(R^3, R^6 及び R^7 は同じであっても異なっていてもよい)

$\text{R}^4, \text{R}^9: -(\text{CH}_2)_m-\text{CH}_3$

$\text{R}^5: \text{OH}, \text{COOH}, -\text{CH}=\text{CH}_2, -\text{C}=\text{CH}_3, -(\text{CH}_2)_z-\text{CH}_3$

$l: 1 \sim 15$

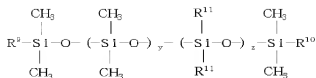
$m, n: 0 \sim 15$

$w: 1 \sim 50$

$x: 1 \sim 300$

[0028]

[Chemical formula 4]



$\text{R}^9, \text{R}^{10}: -\text{OH}$ $\text{R}^{12} - \text{OH}$ $\text{R}^{13} - \text{COOH}$

(R^9 及び R^{10} は同じであっても異なってもよい)

$\text{R}^{11}: -\text{CH}_3, -\text{C}_6\text{H}_5$

$\text{R}^{12}, \text{R}^{13}: -(-\text{CH}_2 -)_p -$

$p: 1 \sim 15$

$y: 1 \sim 200$

$z: 0 \sim 100$

[0029]When the bond strength of carbon black to the particle surface of zinc oxide grains is taken into consideration, the end carboxylic acid conversion polysiloxane to which conversion of polysiloxane, polyether conversion polysiloxane, and the end which have a methylhydrogensiloxane unit was carried out with carboxylic acid is preferred.

[0030]The coating volume of the organosilane compound generated from alkoxysilane, or polysiloxane Organosilane compound covering zinc oxide particle powder, Or it is preferred that it is 0.02 to 5.0 weight % in Si conversion to polysiloxane coating zinc oxide particle powder, it is 0.03 to 4.0 weight % more preferably, and is 0.05 to 3.0 weight % further more preferably.

[0031]It is difficult for less than 0.02weight % of a case to make carbon black of one or more weight sections adhere to zinc oxide particle powder 100 weight section. Since 1-100 weight-section adhesion of the carbon black can be carried out to zinc oxide particle powder 100 weight section when exceeding 5.0 weight %, there is no meaning covered more than needed.

[0032]Carbon black, such as furnace black, channel black, and acetylene black, can be used for carbon black in this invention.

[0033]The coating weight of carbon black is one to 100 weight section to zinc oxide grain 100 weight section.

[0034]In the case of less than one weight section, since the surface activity of zinc oxide grains cannot be controlled, as for the resin composition produced by blending this, mechanical strength falls. In exceeding 100 weight sections, in order to make carbon black adhere to the particle surface of zinc oxide grains via the organosilane compound or polysiloxane generated from alkoxysilane, very big mechanical shearing force is needed, and it becomes disadvantageous industrially.

[0035]It is greatly dependent on the particle shape and grain size of zinc oxide grains which are a core particle, and the particle shape and grain size of composite particle powder in this invention have the shape of particle similar to a core particle.

[0036]That is, 0.01-10.0 micrometers of mean particle diameter [0.015-7.5 micrometers of] of the composite particle powder in this invention are 0.02-5.0 micrometers more preferably.

[0037] Since grain size is too large when the mean particle diameter of the composite particle powder in this invention exceeds 10.0 micrometers, mechanical strength falls [the resin composition produced by blending this]. When mean particle diameter is less than 0.01 micrometer, dispersion into a resin composition may become difficult.

[0038] the BET specific surface area value of the composite particle powder in this invention has preferred $1.0\text{--}500\text{-m}^2/\text{g}$ -- more -- desirable -- $1.5\text{--}400\text{-m}^2/\text{g}$ -- it is $2.0\text{--}300\text{-m}^2/\text{g}$ further more preferably. When a BET specific surface area value is less than $1.0\text{-m}^2/\text{g}$, grains are big and rough, or it has become the grains which sintering produced grains and between grains, and, as for the resin composition produced by blending this, mechanical strength falls.

[0039] 20% or less of the desorption rate of carbon black of the composite particle powder in this invention is desirable, and is 15% or less more preferably. Since uniform dispersion in a resin composition is checked by the carbon black from which it was desorbed when the desorption rate of carbon black exceeds 20%, mechanical strength falls [the resin composition obtained].

[0040] In the valuation method mentioned later, in a ΔE^* value, as for the lightfastness of the composite particle powder in this invention, 5.0 or less are preferred, and it is 4.0 or less more preferably.

[0041] As for the angle of repose of the composite particle powder in this invention, 45 degrees or less are preferred, and it is 40 degrees or less more preferably.

[0042] 2% or less of the degree of surface activity of the composite particle powder in this invention is desirable by the valuation method mentioned later, and is 1.5% or less more preferably.

[0043] Next, the resin composition concerning this invention is described.

[0044] [the dispersion state by visual observation of the resin composition concerning this invention] 4 by a back appearance appraisal method, or 5 -- it being 5 preferably and 5.0 or less. [the light-fast ΔE^* value of a resin composition] Are 4.0 or less preferably, pull and hardness More than $5.0 \times 10^6 \text{Pa}$. Are more than $1.0 \times 10^7 \text{Pa}$ preferably, and the rate of the discoloration portion at the time of heating for 30 minutes at 190 °C aging resistance 5% or less, It is 0% preferably, the percentage of the discoloration portion at the time of heating for 60 minutes is 5% or less preferably 10% or less, and the percentage of the discoloration portion at the time of heating for 120 minutes is 10% or less preferably 15% or less.

[0045] If the blending ratio of the composite particle powder in the resin composition concerning this invention can be used in the range of 0.01 to 200 weight section to resin 100 weight section and handling of a resin composition is taken into consideration, it will be 0.1 to 100 weight section still more preferably 0.05 to 150 weight section preferably.

[0046] As a composition substrate in the resin composition concerning this invention, additives, such as lubricant, a plasticizer, an antioxidant, an ultraviolet ray absorbent, and various stabilizers, are blended by necessity with composite particle powder and well-known thermoplastics.

[0047] As resin, polyolefines, such as polyethylene, polypropylene, polybutene, and polyisobutylene, Polyvinyl chloride, polymethylpentene, polyethylene terephthalate, Polybutylene terephthalate, polystyrene, a styrene acrylic ester copolymer, A styrene vinyl acetate copolymer, acrylonitrile-butadiene-styrene copolymer, An acrylonitrile EPDM-styrene copolymer, acrylic resin, Thermoplastics, such as polyamide,

polycarbonate, polyacetal, and polyurethane, a rosin denaturation maleic resin, a phenol resin, an epoxy resin, polyester resin, silicone resin, rosin ester, rosin, natural rubber, synthetic rubber, etc. can be used.

[0048]The total amount of composite particle powder and an additive of the quantity of an additive should just be 50 or less weight % to resin. When the total amount of the content of an additive and composite particle powder exceeds 50 weight %, moldability falls.

[0049]The resin composition concerning this invention mixes composite particle powder with a resin raw material well beforehand, Next, after adding strong shearing under heating using a kneading machine or an extruder, destroying the floc of composite particle powder and distributing composite particle powder uniformly in a resin composition, it is used for it, carrying out a fabrication to the shape according to the purpose.

[0050]Next, the manufacturing method of the composite particle powder in this invention is described.

[0051]The composite particle powder in this invention mixes zinc oxide particle powder, alkoxyisilane, or polysiloxane, and covers the particle surface of zinc oxide particle powder with alkoxyisilane or polysiloxane, and it ranks second, It can obtain by mixing the zinc oxide particle powder and carbon black which were covered with alkoxyisilane or polysiloxane.

[0052][covering by the alkoxyisilane or polysiloxane to a particle surface of zinc oxide particle powder] What is necessary is just to carry out mixed churning mechanically, carrying out mixed churning of the solution or polysiloxane of zinc oxide particle powder and alkoxyisilane mechanically, or spraying the solution or polysiloxane of alkoxyisilane on zinc oxide particle powder. As for the added alkoxyisilane or polysiloxane, the whole quantity is mostly covered by the particle surface of zinc oxide particle powder.

[0053]The covered alkoxyisilane may be covered as an organosilane compound which is generated when the part passes through a coating process and which is generated from alkoxyisilane. Also in this case, adhesion of subsequent carbon black is not influenced.

[0054]In order to cover alkoxyisilane or polysiloxane to the particle surface of zinc oxide particle powder uniformly, it is preferred to unravel condensation of zinc oxide particle powder using a grinder beforehand.

[0055]Zinc oxide particle powder, alkoxyisilane, or mixed churning with polysiloxane, [as an instrument for carrying out mixed churning with carbon black and the zinc oxide particle powder with which alkoxyisilane or polysiloxane is covered by the particle surface] The device which can apply shearing force to a powder bed is preferred, especially, a shear and the knife device which comes out and can compress simultaneously, for example, a wheel type kneading machine, a ball type kneading machine, a blade type kneading machine, and a roll-die kneading machine can be used, and a wheel type kneading machine can use it more effectively.

[0056]as said wheel type kneading machine -- an edge runner (a "mix muller".) With "SHIMPUSOMMIRU", a "sand mill", and synonymous words, a certain multi-Mull, There are SUTOTTSUMIRU, a wet pan mill, KONAMIRU, a ring muller, etc., it is an edge runner, multi-Mull, SUTOTTSUMIRU, wet pan mill, and ring muller preferably, and he is an edge runner more preferably. There are a vibration mill etc. as said ball type kneading machine. As said blade type kneading machine, there are a Henschel mixer, a

planetary mixer, a NAUTA mixer, etc. There are an extruder etc. as said roll-die kneading machine.

[0057][the conditions at the time of mixed churning with zinc oxide particle powder, alkoxyasilane, or polysiloxane] So that alkoxyasilane or polysiloxane may be covered as uniformly as possible by the particle surface of zinc oxide particle powder, Preferably line load 19.6 to 1960 N/cm (2 - 200 kg/cm) 98 - 1470 N/cm (10 - 150 kg/cm), 147 - 980 N/cm (15 - 100 kg/cm) and the processing time should just adjust a processing condition suitably in 10 minutes - 20 hours preferably for 5 minutes - 24 hours. The rate of stirring should just adjust suitably 2-2000 rpm of processing conditions [5-1000 rpm of] in 10-800 rpm more preferably.

[0058]The loadings of alkoxyasilane or polysiloxane has 0.15 to 45 preferred weight section to zinc oxide particle powder 100 weight section. By the loadings of 0.15 to 45 weight section, 1-100 weight-section adhesion of the carbon black can be carried out to zinc oxide particle powder 100 weight section.

[0059]After covering alkoxyasilane or polysiloxane to the particle surface of zinc oxide particle powder, carbon black is added, mixed churning is carried out, and carbon black is made to adhere to alkoxyasilane or polysiloxane coating. Desiccation thru/or heat-treatment may be performed further as occasion demands.

[0060]carbon black -- a small quantity -- every -- or [adding over 5 minutes - about 20 hours for 5 minutes - 24 hours preferably especially, spending many hours] -- or, It is preferred to divide and to add carbon black of five to 25 weight section to zinc oxide particle powder 100 weight section, until it becomes desired loadings.

[0061]So that carbon black may adhere uniformly, [the conditions which can be set at the time of mixed churning] Preferably line load 19.6 to 1960 N/cm (2 - 200 kg/cm) 98 - 1470 N/cm (10 - 150 kg/cm), 147 - 980 N/cm (15 - 100 kg/cm) and the processing time should just adjust a processing condition suitably in 10 minutes - 20 hours preferably for 5 minutes - 24 hours. The rate of stirring should just adjust suitably 2-2000 rpm of processing conditions [5-1000 rpm of] in 10-800 rpm more preferably.

[0062]The loadings of carbon black is one to 100 weight section to zinc oxide particle powder 100 weight section, and is five to 90 weight section more preferably three to 95 weight section.

[0063]Since the surface activity of zinc oxide grains cannot be controlled when the loadings of carbon black is less than one weight section, mechanical strength falls [the resin composition produced by blending this]. In exceeding 100 weight sections, in order to make carbon black adhere to the particle surface of zinc oxide grains via the organosilane compound or polysiloxane generated from alkoxyasilane, very big mechanical shearing force is needed, and it becomes disadvantageous industrially.

[0064]As for the cooking temperature in the case of performing desiccation thru/or heat-treatment, 40-150 °C is usually preferred, and it is 60-120 °C more preferably, and the heat time of 10 minutes - 12 hours is preferred, and is more preferred. [of 30 minutes - 3 hours]

[0065]When alkoxyasilane is used, by passing through these processes, it becomes an organosilane compound eventually generated from alkoxyasilane, and is covered.

[0066]

[Mode for carrying out the invention]The typical embodiment of this invention is as follows.

[0067]Each mean particle diameter of grains measured the particle diameter of 350 grains shown in an electron microscope photograph, respectively, and showed it by the average.

[0068]The value measured by the BET adsorption method showed the specific surface area value.

[0069]Each of the amount of Si(s) contained in the organosilane compound or polysiloxane generated from the alkoxysilane of composite particle powder used the "X-ray fluorescence device 3063M type" (made by Rigaku Industrial Corp.), and measured it according to the "X-ray-fluorescence-analysis general notices" of JIS K0119.

[0070]The coating volume of carbon black adhering to composite particle powder was calculated by measuring a carbon content using "Horiba metal carbon and sulfur analyser EMIA-2200 type" (made by HORIBA LTD.).

[0071]The value calculated by the following method showed the desorption rate (%) of carbon black adhering to composite particle powder. It is shown that there are so few amounts of desorption of carbon black from the particle surface of composite particle powder that the desorption rate of carbon black is close to 0%.

[0072]After putting the particle powder 3g under test and 40 ml of ethanol into a 50-ml sedimentation pipe and performing ultrasonic dispersion for 20 minutes, it settled for 120 minutes and specific gravity difference separated particle powder under test and the carbon black from which it was desorbed. Subsequently, 40 ml of ethanol was again added to the separated particle powder under test, further, after performing ultrasonic dispersion for 20 minutes, it settled for 120 minutes and specific gravity difference separated particle powder under test and the carbon black from which it was desorbed. This particle powder under test was dried at 100 °C for 1 hour, the carbon content was measured using above-mentioned "Horiba metal carbon and sulfur analyser EMIA-2200 type" (made by HORIBA LTD.), and the value calculated according to the following formula was made into the desorption rate (%) of carbon black.

[0073]

[Mathematical formula 1]Desorption rate (%) = $\{(W_a - W_e) / W_a\} \times 100$ Wa of carbon black: Carbon black coating weight of the composite particle powder after the carbon black coating weight We:desorption test of composite particle powder [0074]The angle of repose (degree) of composite particle powder measured using the "powder circuit tester" (made by HOSOKAWA MICRON CORPORATION). It is shown that the flowability of composite particle powder is excellent, so that an angle of repose is small.

[0075]The degree of surface activity of composite particle powder was evaluated by measuring the amount of residual solvents shown below.

[0076]The sample powder 1g and 10 g of solvents (MEK) First, after [**** picking, after being immersed for 3 hours], It was air-dry for 24 hours, and further, it dried at 60 °C for 24 hours, the carbon quantity of the sample powder after desiccation was measured using "Horiba metal carbon and sulfur analyser EMIA-2200 type" (made by HORIBA LTD.), and residual carbon quantity was quantified and calculated. There is so little survival of a solvent that there is little residual carbon quantity, and it is shown that the surface activity of fine particles is controlled.

[0077][the lightfastness of zinc oxide particle powder, carbon black, and composite particle powder] The elementary color enamel produced in accordance with the method of mentioning later is applied to a cold rolled steel plate (0.8mmx70mmx150mm) (JIS G-3141) by a thickness of 150 micrometers, The half of the piece for measurement of

spreading obtained by drying and forming a paint film is covered with metal foil. An "eye super UV tester" (SUV-W13 (made by IWASAKI ELECTRIC CO. LTD.)) is used. After carrying out the continuation exposure of the ultraviolet radiation by exposure hardness 100 mW/cm² for 6 hours. By covering with metal foil, the hue (an L* value, an a* value, a b* value) of the portion with which ultraviolet radiation was not irradiated, and the portion which carried out UV irradiation was measured, respectively, and the deltaE* value computed according to the two following showed on the basis of the measured value of the portion with which ultraviolet radiation was not irradiated.

[0078]

[Mathematical formula 2] $\Delta E^* \text{ value} = (\Delta L^* \text{ value})^2 + (\Delta a^* \text{ value})^2 + (\Delta b^* \text{ value})^2$; Difference ΔL^* value of the L* value of the UV irradiation existence of the sample to compare: Difference Δa^* value of the a* value of the UV irradiation existence of the sample to compare: . The difference of the b* value of the UV irradiation existence of the sample to compare [0079] Production of elementary color enamel : Blend the above-mentioned sample fine particles 10g, the amino alkyl resin 16g, and the thinner 6g, and it adds and ranks second to a 140-ml glass bottle with the 3 mmphi glass bead 90g. After carrying out mixture dispersion for 45 minutes with a paint shaker, added the amino alkyl resin 50g, and also the paint shaker was made to distribute for 5 minutes, and elementary color enamel was produced.

[0080] The lightfastness of a resin composition covers the half of the resin plate produced by the method of mentioning later with metal foil. An "eye super UV tester" (SUV-W13 (made by IWASAKI ELECTRIC CO. LTD.)) is used. After carrying out the continuation exposure of the ultraviolet radiation by exposure hardness 100 mW/cm² for 6 hours. By covering with metal foil, the hue (an L* value, an a* value, a b* value) of the portion with which ultraviolet radiation was not irradiated, and the portion which carried out UV irradiation was measured, respectively, and the deltaE* value computed according to said two number showed on the basis of the measured value of the portion with which ultraviolet radiation was not irradiated.

[0081] The dispersibility to the resin composition of composite particle powder judged the number of the floc which is not distributed in the obtained precolored resin plate surface by viewing, and evaluated it in five steps. 5 shows that a dispersion state is the best.

5: Less than 5 more than per piece per undistributed thing private seal **** and 4: 1-cm², less than five or more 10 per 3: 1-cm², less than ten or more 50 per 2: 1-cm², and 50 or more per 1: 1-cm²

[0082] The resin composition pulled, and hardness produced and measured the No. 1 specimen according to JIS K7113.

[0083] When the precolored resin plate (1.5 cm by 1.5 cm x 1 mm in thickness) which scoured composite particle powder is heated at 190 **, [aging resistance] the ratio of the area S of the portion which it became and into which resin deteriorated, and surface area S₀ (1.5x1.5= 2.25-cm²) of the coloring plate before heating -- it asked by mincing S/S₀ 5%, coming out and quantifying.

[0084] That is, when x(S/S₀) 100 is 0%, the state where there is no deterioration is shown, and when x(S/S₀) 100 is 100%, the state where resin deteriorated completely is shown.

[0085] <Manufacture of composite particle powder> zinc oxide particle powder (particle shape): [grain form and mean particle diameter of 1.012 micrometers] BET specific surface area value 3.3m²/g and light-fast deltaE* value 5.24 11.0kg were supplied to the

edge runner "MPUV-2 type" (a product name, made in a Matsumoto, Inc. casting iron factory), mixed churning was performed for 30 minutes by 294 N/cm (30 kg/cm), and condensation of grains was unraveled lightly.

[0086] next the methyltriethoxysilane solution produced by carrying out mixed dilution of 110 g of the methyltriethoxysilane (trade name: made by two-stage-liquefaction8123;GE Toshiba Silicones Co., Ltd.) by 200 ml of ethanol] It added to the above-mentioned zinc oxide particle powder, working an edge runner, and mixed churning was performed for 30 minutes by the line load of 588 N/cm (60 kg/cm). The rate of stirring at this time was performed at 22 rpm.

[0087]Next, the black pigment A (kind:) [carbon black, particle shape:grain form, and mean particle diameter of 0.02 micrometer] [BET specific surface area value 134.0m²/g and light-fast deltaE* value 12.65 1,650g] Apply for 10 minutes, and add, working an edge runner, and also by the line load of 392 N/cm (40 kg/cm) For 20 minutes, After performing mixed churning and making carbon black adhere after methyltriethoxysilane covering, heat-treatment was performed for 60 minutes at 105 ** using the dryer, and composite particle powder was obtained. The rate of stirring at this time was performed at 22 rpm.

[0088]The obtained composite particle powder was granular particle powder whose mean particle diameter is 1.015 micrometers. As for 12.5m²/g and an angle of repose, 0.82 and the light-fast deltaE* value of 37 degrees and the degree of surface activity were [BET specific surface area value] 2.09, and the desorption rate of carbon black was 7.4%. The coating volume of the organosilane compound generated from methyltriethoxysilane was 0.15 weight % in Si conversion, and the quantity of adhering carbon black was 12.99 weight % (it is equivalent to 15 weight sections to zinc oxide particle powder 100 weight section) in C conversion.

[0089]Since the black pigment A was hardly accepted as a result of electron microscope photograph observation, having adhered to organosilane compound covering of the black pigment A which the whole quantity generates from methyltriethoxysilane mostly was admitted.

[0090]<Manufacture which is a resin composition> The weighing capacity of said composite particle powder 2.0g and 8D(made by ZEON CORPORATION) 47.5 g of the polyvinyl-chloride-resin powder 103EPs was carried out, these were put into the 100-ml poly beaker, it mixed well with the spatula, and powder mixture was obtained. [0091]Add 0.5g of calcium stearate to the obtained powder mixture, and it mixes, After continuing kneading until it scoured said powder mixture with a roll little by little and the resin composition was united, after setting the clearance of the roll between heat heated at 160 ** as 0.2 mm, it exfoliated from the roll and the resin composition was used as a precolored resin plate raw material.

[0092]Next, it put in in the hot press heated at 180 ** on both sides of the above-mentioned resin composition between the stainless plates by which the surface polish was carried out, pressing was carried out by the pressure of 98,000kPa (1-ton [cm] ²), and the 1-mm-thick precolored resin plate was obtained. The dispersion state of the obtained precolored resin plate was 5, and the percentage of the portion of having discolored lightfastness with the deltaE* value when it pulls and heats at hardness 1.4x10⁷Pa and 190 **, 2.31 and was 5% or less, when it heated for 30 minutes, it heated for 60 minutes 0% and it heated for 120 minutes 0%.

[0093]

[Function]The most important point is covered with the organosilane compound or polysiloxane which the particle surface of zinc oxide particle powder generates from alkoxy silane in this invention, and. The resin composition which blended with this covering the composite particle powder to which carbon black has adhered is the fact of excelling in mechanical strength, lightfastness, and aging resistance.

[0094]I think that it is because the composite particle powder which consists of zinc oxide particle powder which has ultraviolet absorption ability, and carbon black was used as a Reason the lightfastness of the resin composition concerning this invention is excellent, as a filler blended into a resin composition.

[0095]As a Reason the aging resistance of the resin composition concerning this invention is excellent, this invention person thinks as follows. Usually, since it has a catalysis of photooxidation, surface activity is high and promotes aging of resin, but. [the zinc oxide particle powder blended into the resin composition as a vulcanization accelerator] [the composite particle powder blended with the resin composition concerning this invention] In order to make the carbon black which has a function as an anti-oxidant adhere to the particle surface of zinc oxide grains via the organosilane compound or polysiloxane generated from alkoxy silane, I reduced the surface activity of zinc oxide grains, and, as a result, think that deterioration of resin has been controlled.

[0096]this invention person thinks as follows as a Reason the mechanical strength of the resin composition concerning this invention is excellent. Generally, [the carbon black blended into the resin composition as a reinforcer] In order to originate in being particles and to usually carry out an action as floc, the dispersibility in the inside of a resin composition is bad, Although sufficient reinforcing effect cannot be acquired, [the composite particle powder blended with the resin composition of this invention] In order to make carbon black adhere to the particle surface of zinc oxide grains with comparatively easy dispersion via the organosilane compound or polysiloxane generated from alkoxy silane, dispersion in a resin composition is easy, and. By unevenness arising in a particle surface by carbon black adhering to the particle surface of zinc oxide grains, and as a result controlling the field contact between composite particles, the dispersibility in the inside of a resin composition improved, and I think that the reinforcing effect has been demonstrated effectively.

[0097]

[Working example]Next, an embodiment and a comparative example are shown.

[0098]Core particles 1-3: The zinc oxide particle powder and hematite particle powder which have characteristics shown in Table 1 as core particle powder were prepared.

[0099]

[Table 1]

芯粒子 の種類	芯粒子粉末の特性				
	種類	形状	平均 粒子径 (μm)	BET比 表面積値 (m^2/g)	耐光性 ΔE^* 値 (-)
芯粒子1	酸化亜鉛	粒状	0.183	18.3	5.86
# 2	#	#	0.321	3.2	5.16
# 3	ヘマタイト	#	0.383	1.6	6.52

[0100]Black pigment: Carbon black and aniline black which have various characteristics shown in Table 2 as a black pigment were prepared.

[0101]

[Table 2]

黒色顔料	黒色顔料の特性				
	種類	粒子 形状	平均 粒径 (μm)	BET比 表面積値 (m^2/g)	耐光性 ΔE^* 値 (-)
A	カーボンブラック	粒状	0.02	134.0	12.65
B	アニリンブラック	棒状	0.31	56.8	15.21

[0102]Composite particles 1-8 : The kind of additive in the coating process by the kind, alkoxysilane, or polysiloxane of a core particle, Composite particle powder was obtained like said embodiment of the invention except having changed various line loads and time of the kind of black pigment in the line load of loadings and edge runner treatment and time, and the adhesion process of a black pigment, loadings, and edge runner treatment.

[0103]The various characteristics of the composite particle powder obtained in Table 3 in the conditions of manufacture at this time are shown in Table 4.

[0104]

[Table 3]

複合粒子	芯粒子の種類	複合顔料の製造									
		糊剤による被覆工程					黒色顔料の付着工程				
		添加物		エッジランナー処理		被覆量	黒色顔料		エッジランナー処理		付着量
		種類	添加量 (重量部)	線荷重 (N/cm)	時間 (min)	(S)換算 (重量%)	種類	添加量 (重量部)	線荷重 (N/cm)	時間 (min)	(C)換算 (重量%)
複合粒子1	n 1	メチルメタクリレート	1.0	588	60	0.15	A	50.0	588	60	33.19
		メチルヘキシルアクリレート	0.5	588	60	0.20	A	10.0	588	60	9.02
		フェニルメタクリレート	1.0	392	40	0.14	A	5.0	392	40	4.68
		メチルメタクリレート	2.0	588	60	0.31	A	10.0	588	60	9.04
		メチルメタクリレート	1.0	588	60	0.15	B	10.0	588	60	7.41
		---	---	---	---	---	A	10.0	588	60	9.00
		メチルメタクリレート	1.0	588	60	0.15	---	---	---	---	---

[0105]

[Table 4]

複合粒子	複合粒子粉末の特性					
	平均 粒子径 (μm)	BET比 表面積値 (m^2/g)	安息角 ($^\circ$)	表面 活性度 (%)	耐光性 ΔE^* 値 (-)	カーボンブラック の脱離率 (%)
複合粒子1	0.185	15.3	36	0.65	1.90	8.6
＃ 2	0.163	14.6	37	0.74	2.02	7.4
＃ 3	0.321	3.6	38	0.82	2.16	5.9
＃ 4	0.363	3.1	39	0.98	2.20	7.0
＃ 5	0.183	16.3	39	2.23	2.18	8.2
＃ 6	0.183	24.5	48	2.18	5.65	64.6
＃ 7	0.183	18.6	49	2.59	5.74	---

[0106]The <resin-composition> embodiments 1-3, the comparative examples 1-7: The resin composition was obtained like said embodiment of the invention except having changed the kind of bulking agent to composite particle powder, the core particle, and the black pigment variously.

[0107]The conditions of manufacture at this time and the acquired various characteristics of a resin composition are shown in Table 5.

[0108]

[Table 5]

実施例 及び 比較例	樹脂組成物 の製造 充填剤 の種類	樹脂組成物の特性					
		分散 状態 (-)	耐光性 ΔE^* 値 (-)	引張り 強度 (Pa)	190℃で加熱した場合に劣 化変色した部分の面積割合 (%)		
					30分	60分	120分
実施例1	複合粒子1	5	2.08	17.8×10^6	0	0	0
# 2	# 2	5	2.24	12.6×10^6	0	0	5
# 3	# 3	5	2.36	11.5×10^6	0	5	10
比較例1	芯粒子1	2	6.13	2.4×10^6	10	15	25
# 2	# 2	2	5.35	2.6×10^6	10	15	20
# 3	黒色顔料A	1	8.44	4.1×10^6	0	0	5
# 4	複合粒子4	4	2.48	1.3×10^6	0	5	10
# 5	# 5	4	2.39	3.2×10^6	10	15	25
# 6	# 6	1	5.81	3.0×10^6	10	15	25
# 7	# 7	2	5.92	2.7×10^6	5	15	20

[0109]

[Effect of the Invention]The resin composition containing the composite particle powder concerning this invention is preferred as a resin composition which has the outstanding mechanical strength, lightfastness, and aging resistance.

[Translation done.]